Multidimensional femtosecond spectroscopies of molecular aggregates and semiconductor nanostructures: The nonlinear exciton equations

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A unified description of nonlinear optical spectroscopies of molecular aggregates (starting with the Frenkel-Heitler-London Hamiltonian) and semiconductors (starting with the two-band model) is developed using the nonlinear exciton equations (NEE). The equations follow explicitly the complete set of one-, two-, and three-point dynamical exciton variables relevant for the third-order response. Effects of nuclear motions are incorporated through relaxation superoperators calculated perturbatively in exciton-phonon coupling. A Green's function expression for the third-order response is derived by solving the NEE using a new truncation scheme based on factorizing the three-point relaxation kernels. These results set the stage for designing multidimensional spectroscopies of excitons and analyzing them using coherence-transfer pathways. © *1998 American Institute of Physics.* [S0021-9606(98)70545-8]

I. INTRODUCTION

The dynamics of electronic excitations in assemblies of coupled molecular chromophores (crystals, nanostructures and aggregates) and semiconductor systems (bulk, quantum dots, quantum wells, and superlattices) can be effectively probed using femtosecond spectroscopic techniques. Hole-burning,[1,2] pump-probe,[3,4] fluorescence depolarization,[5] photon echoes[6] and four-wave mixing have been applied to molecular aggregates such as J-aggregates[7–9] and biological light-harvesting complexes[10,11] and to semiconductor materials as well.[12,13]

Despite the different structure of electronic excitations, these two classes of materials share several important fundamental similarities, allowing the description of their dynamics and optical response within the same framework.[13,14] First, in both systems the elementary electronic excitations are excitons: Femtosecond techniques probe the interplay of coherent and incoherent dynamics, elastic and inelastic scattering as well as self-trapping of excitons. The Wannier-type excitons in semiconductors are formed by an electron in the conduction band and a hole in the valence band. Molecular excitations moving coherently across the system are known as Frenkel excitons. These can also be considered as electron-hole pairs with the constraint that the electron and the hole must belong to the same molecule at all times. This implies that there is no conceptual difference between the two types of materials. It should be noted, however, that due to the absence of intermolecular charge transfer in molecular assemblies, the number of Frenkel one-exciton states scales $\sim N$ with the number of molecules N, whereas the number of Wannier excitons (hereafter we refer to all electron-hole pair states as excitons regardless of whether their relative motion is bound or not) scales $\sim N^2$. Similarly, the number of two-exciton states scales $\sim N^2$ and $\sim N^4$, respectively. Although

the difference is rather technical than conceptual, it has crucial implications on adopting the right algorithm for numerical calculations. In general, a higher level of theory which, e.g., accounts for the structure of two-exciton resonances can be much more easily used in the modeling of molecular nanostructures compared with their semiconductor counterparts.

Another important similarity is that both systems are well described by a material Hamiltonian that conserves the number of electron-hole pairs. Non-pair-conserving processes are controlled by the ratio of the exciton binding energy (in semiconductors) or the intermolecular coupling (in molecular aggregates) to the optical frequency, which is typically small in both systems. This simplifies the original many-body problem considerably, since the energy spectrum consists of well-separated groups of energy levels representing single, double excitations, etc. Because only the radiation field can change the number of electron-hole pairs, we can classify optical techniques according to their power dependence on the incoming fields, and find that very few types of electronic excitations need to be considered at each order. This provides a convenient computational scheme as well as a basis for an intuitive physical picture.[15]

The simplest way to include the coupling with vibrational (phonon) degrees of freedom is by eliminating the nuclear variables and incorporating their effects through relaxation superoperators. In molecular aggregates this results in the Redfield equation for the reduced exciton density matrix,[16,17] whereas for a semiconductor system it yields the semiconductor Bloch equations (SBE) with dephasing,[12] which form a basic tool for calculating optical signals in superlattices using realistic anisotropic three-dimensional models.[18]

In the absence of coupling to phonons it is possible to derive equations of motion for one- and two-exciton variables[19] which avoid the explicit calculation of two-

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exciton states, tracing the origin of the third-order nonlinear optical response to exciton-exciton scattering.[20,21] Phonon-induced dephasing has been incorporated into the theories of $\chi^{(3)}$ in molecular aggregates by including additional exciton-population variables and applying certain factorization schemes for closing the equations.[22,23] This level of theory is equivalent to the SBE with dephasing for semiconductors. The resulting expressions for $\chi^{(3)}$ describe adequately transient grating experiments, however, they do not apply when both exciton transport and two-exciton resonances are important, as may be the case in pump-probe and photon echo spectroscopies. A Green's function approach which describes the combined effects of exciton transport and two-exciton resonances has been developed[24] and applied to various spectroscopies in J-aggregates,[24] pump-probe spectroscopy of light harvesting antenna complexes,[25] photon-echoes[26] and four wave mixing.[27] In the absence of vibronic coupling the method was extended to molecular aggregates made of three-level molecules[28] and to semiconductors.[14,29] Effects of strong coupling to phonons can be incorporated in equations of motion describing polaron transport[17,30,31] or by solving equations of motion for reduced wave packets which involve the dynamics of a few important collective nuclear coordinates.[32] These extensions will not be considered here.

The relevant dynamical variables for third order spectroscopies in aggregate made out of two-level molecules have been identified in Refs. 15 and 21. In the present work we generalize these earlier studies in several ways. First, we outline a procedure that holds for multilevel molecules. There is a great freedom in the choice of exciton variables and we demonstrate how it may be used to simplify the theoretical analysis through a nonlinear transformation of the dynamical variables. Second, we consider a model of a linearly coupled phonon bath and derive closed expressions for the relaxation superoperators to second order in exciton-phonon coupling. The resulting nonlinear exciton equations of motion (NEE) provide the basic theoretical framework that applies to semiconductor nanostructures as well. Third, a closed-form Green's function expression for the nonlinear response is derived by solving the NEE using a new approximation based on factorizing some of the relaxation superoperators. The resulting expression generalizes and unifies many of the earlier studies. Although spontaneous light emission (fluorescence) is not considered here, it can be calculated as well using the present theory.

This paper is organized as follows. In Sec. II we present a general Hamiltonian representing an aggregate made out of multilevel molecules. The Hamiltonian written using collective exciton variables contains three types of nonlinearities: direct Coulombic intermolecular interactions, nonboson statistics (nonlinear commutation relations between exciton operators) and nonlinearities in the dipole operator. In Appendixes A and B we show how the conventional Hamiltonians representing an aggregate of multilevel molecules, and the two band model of semiconductors can be transformed, respectively, to assume the form of our general Hamiltonian. We then derive the NEE which depend on phonon-induced relaxation superoperators defined formally in Appendix D.

The NEE are simplified considerably by an approximate calculation of the relaxation terms. These equations are then solved in Sec. III, resulting in a closed-form Green's function expression for the third-order response. Our results are finally discussed in Sec. IV.

II. COLLECTIVE EXCITON VARIABLES AND THE NONLINEAR EXCITON EQUATIONS

The starting point for our analysis is the Frenkel exciton Hamiltonian with the Heitler-London approximation for molecular aggregates (Appendix A), and the two-band Hamiltonian for semiconductors (Appendix B). These Hamiltonians neglect processes which do not conserve the number of excitons, which is justified since in both systems the exciton frequencies are much larger than the exciton interactions.

The central result of this section is a unified representation of the Frenkel-exciton and the Wannier-exciton Hamiltonians including the coupling to nuclear motions. The linear optical response only probes one-exciton states, whereas the third-order optical nonlinearity involves two-exciton states as well. Our unified material exciton Hamiltonian which describes the optical response of both systems up to third order is given by the sum of the electronic part H_e, the vibrational Hamiltonian H_{ph} and the vibronic coupling H_{int}

$$H = H_e + H_{ph} + H_{int}. \tag{2.1}$$

These have the following form in terms of the exciton annihilation (creation) operators $\hat{B}_n (\hat{B}_n^\dagger)$ and nuclear coordinates q_α

$$H_e = \sum_{mn} h_{mn} \hat{B}_m^\dagger \hat{B}_n + \sum_{mnkl} U_{mn,kl} \hat{B}_m^\dagger \hat{B}_n^\dagger \hat{B}_k \hat{B}_l, \tag{2.2}$$

$$H_{ph} = \sum_\alpha \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2 q_\alpha^2}{2} \right), \tag{2.3}$$

$$H_{int} = \sum_{mn\alpha} \bar{h}_{mn,\alpha} \hat{B}_m^\dagger \hat{B}_n q_\alpha + \sum_{mnkl\alpha} \bar{U}_{mn,kl;\alpha} \hat{B}_m^\dagger \hat{B}_n^\dagger \hat{B}_k \hat{B}_l q_\alpha, \tag{2.4}$$

In Eqs. (2.2)–(2.4) h_{mn} represents the one-exciton Hamiltonian, $U_{mn,kl}$ describes the exciton-exciton interactions, m_α and ω_α are the reduced masses and frequencies of nuclear modes, $\bar{h}_{mn,\alpha}$ and $\bar{U}_{mn,kl;\alpha}$ stand for vibronic coupling which originates from the q_α-dependence of h_{mn} and $U_{mn,kl}$, respectively. The commutation relations for the exciton operators have the form

$$[\hat{B}_m, \hat{B}_n^\dagger] = \delta_{mn} - 2 \sum_{kl} \mathcal{P}_{mk,nl} \hat{B}_k^\dagger \hat{B}_l, \tag{2.5}$$

where $\mathcal{P}_{mk,nl}$ is a tetradic matrix which describes the deviation of the exciton commutation relations from those of bosons. It follows from the Jacobi identity for the commutators that

$$\mathcal{P}_{mn,kl} = \mathcal{P}_{nm,kl} = \mathcal{P}_{mn,lk}. \tag{2.6}$$

The total Hamiltonian representing the system coupled to the optical field $\mathcal{E}(t)$ is

$$H_T = H - \mathcal{E}(t) P, \tag{2.7}$$

and P is the polarization operator

$$P = \sum_n \mu_n^{(1)} \hat{B}_n + \sum_{mkl} \mu_{m,kl}^{(2)} \hat{B}_m^\dagger \hat{B}_k \hat{B}_l + \text{H.c.}, \tag{2.8}$$

where $\mu_n^{(1)}$ and $\mu_{m,kl}^{(2)}$ are the matrix elements of the polarization operator.

In general Eqs. (2.2)–(2.5) contain higher-order products of $\hat{B}_n$ and $\hat{B}_n^\dagger$, however, since they only contribute to the optical response in higher than third order, they are neglected. In Appendix A we show how the general Hamiltonian of a molecular aggregate made out of interacting multi-level molecules linearly coupled to a harmonic phonon bath can be represented in the form of Eqs. (2.2)–(2.5). In Appendix B we introduce the exciton operators for the two-band model of semiconductors and recast it in the form of Eqs. (2.2)–(2.5) as well. All the results of this paper, therefore, apply to both systems. In addition molecular assemblies may often have charge transfer processes (e.g., the photosynthetic reaction center). This intermediate case of charge transfer excitons is also covered by our Hamiltonian.

Now we are in a position to derive a closed system of equations for the exciton variables. To that end, we introduce the following relevant dynamical variables:

$$B_n \equiv \langle \hat{B}_n \rangle, \quad Y_{mn} \equiv \langle \hat{B}_m \hat{B}_n \rangle,$$
$$N_{mn} \equiv \langle \hat{B}_n^\dagger \hat{B}_m \rangle, \quad Z_{mn,j} \equiv \langle \hat{B}_j^\dagger \hat{B}_m \hat{B}_n \rangle, \tag{2.9}$$

which are required to obtain a closed system of equations for the optical response up to third order.[33] The Heisenberg equation of motion $i\, d\hat{B}_m/d\tau = [\hat{B}_m, H_T]$ yields

$$i \frac{d\hat{B}_m}{d\tau} = \sum_n h_{mn}\hat{B}_n + \sum_{nkl} V_{mn,kl}\hat{B}_n^\dagger \hat{B}_k \hat{B}_l - \mathcal{E}_m^{(1)}$$
$$- \sum_{kl} \mathcal{E}_{m,kl}^{(2)} \hat{B}_k^\dagger \hat{B}_l - \sum_{kl} \mathcal{E}_{m,kl}^{(3)} \hat{B}_k \hat{B}_l + [\hat{B}_m, H_{\text{int}}], \tag{2.10}$$

Applying the truncation procedure of Refs. 15, 19, 21, and 34 finally gives

$$i \frac{dB_m}{d\tau} = \sum_n h_{mn}B_n + \sum_{nkl} V_{mn,kl} Z_{kl,n} - \mathcal{E}_m^{(1)}$$
$$- \sum_{kl} \mathcal{E}_{m,kl}^{(2)} N_{lk} - \sum \mathcal{E}_{m,kl}^{(3)} Y_{kl} + \dot{B}_m, \tag{2.11}$$

$$i \frac{dY_{mn}}{d\tau} = \sum_{kl} h_{mn,kl}^{(2)} Y_{kl} - B_m \mathcal{E}_n^{(1)} - B_n \mathcal{E}_m^{(1)}$$
$$- \sum_k \mathcal{E}_{n,mk}^{(2)} B_k + \dot{Y}_{mn}, \tag{2.12}$$

$$i \frac{dN_{ij}}{d\tau} = \sum_m (h_{im}N_{mj} - N_{im}h_{mj}) - \mathcal{E}_i^{(1)} B_j^* + \mathcal{E}_j^{(1)} B_i + \dot{N}_{ij}, \tag{2.13}$$

$$i \frac{dZ_{mn,j}}{d\tau} = \sum_{kl} h_{mn,kl}^{(2)} Z_{kl,j} - \sum_i h_{ij} Z_{mn,i} - \mathcal{E}_m^{(1)} N_{nj}$$
$$- \mathcal{E}_n^{(1)} N_{mj} - \sum_k \mathcal{E}_{m,nk}^{(2)} N_{kj} + \mathcal{E}_j^{(1)} Y_{mn} + \dot{Z}_{mnj}, \tag{2.14}$$

where

$$h_{mn,kl}^{(2)} \equiv \delta_{mk} h_{nl} + h_{mk}\delta_{nl} + V_{mn,kl}, \tag{2.15}$$

$$V_{mn,kl} \equiv 2U_{mn,kl} - 2\sum_p \mathcal{P}_{mn,pk} h_{pl} - 2\sum_{pq} \mathcal{P}_{mn,pq} U_{pq,kl}, \tag{2.16}$$

$$\mathcal{E}_m^{(1)} \equiv \mu_m^{(1)} \cdot \mathcal{E}, \tag{2.17}$$

$$\mathcal{E}_{m,kl}^{(2)} \equiv 2\mu_{l,km}^{(2)} \cdot \mathcal{E} - 2\sum_n \mathcal{P}_{mk,nl}\mu_n^{(1)} \cdot \mathcal{E} - 2\sum_{rs} \mathcal{P}_{mk,rs}\mu_{l,rs}^{(2)} \cdot \mathcal{E}, \tag{2.18}$$

$$\mathcal{E}_{m,kl}^{(3)} \equiv \mu_{m,kl}^{(2)} \cdot \mathcal{E}. \tag{2.19}$$

The variables $\dot{B}, \dot{Y}, \dot{N}$, and $\dot{Z}$ denote relaxation terms which are linear in B, Y, N, and Z. A procedure for evaluating these terms is outlined in Appendixes C and D.

The most time and memory consuming part in solving Eqs. (2.11)–(2.14) is connected with Eq. (2.14) for $Z_{mn,j}$ which contains $\sim N^3$ variables where N is the number of one-exciton states. The corresponding relaxation operator is an $N^3 \times N^3$ matrix. To overcome this bottleneck, we derive in this section a simplified scheme which allows us to reduce the number of variables to $\sim N^2$. To that end we invoke the following approximations for the relaxation terms in Eqs. (2.11)–(2.14). We first neglect the contributions which involve the driving field $\mathcal{E}$. This yields

$$\dot{B}_m = -i\sum_n \Gamma_{mn}B_n, \tag{2.20}$$

$$\dot{Y}_{mn} = -i\sum_{kl} R_{mn,kl}Y_{kl}, \tag{2.21}$$

$$\dot{N}_{ij} = -i\sum_m (\Gamma_{im}N_{mj} + N_{im}\Gamma_{mj}) - i\sum_{mn} \bar{R}_{ij}^{mn} N_{mn}, \tag{2.22}$$

$$\dot{Z}_{mn,j} = -i\sum_{kl} R_{mn,kl}Z_{kl,j} - i\sum_s \Gamma_{sj}Z_{mn,s}$$
$$- i\sum_{kls} \tilde{R}_{mn,j}^{kl,s} Z_{kl,s}. \tag{2.23}$$

We shall refer to $\bar{R}$ and $\tilde{R}$ as the irreducible relaxation operators. $\bar{R}_{ij}^{mn}$ in Eq. (2.22) is responsible for the conservation of the number of excitons and therefore may not be neglected. In the following we neglect the irreducible relaxation operator $\tilde{R}$ in Eq. (2.23):

$$\tilde{R}_{mnj}^{kl,s} = 0. \tag{2.24}$$

Expressions for the relaxation kernels, evaluated to second order in exciton-phonon coupling are presented in Appendix D. Upon the substitution of Eqs. (2.20)–(2.23) into Eqs. (2.11)–(2.14) we obtain

$$i\frac{dB_m}{d\tau} - \sum_n (h_{mn} - i\Gamma_{mn})B_n$$

$$= \sum_{nkl} V_{mn,kl}Z_{kl,n} - \mathcal{E}_m^{(1)} - \sum_{kl} \mathcal{E}_{m,kl}^{(2)}N_{lk} - \sum_{kl} \mathcal{E}_{m,kl}^{(3)}Y_{kl},$$

$$(2.25)$$

$$i\frac{dY_{mn}}{d\tau} - \sum_{kl} (h_{mn,kl}^{(2)} - iR_{mn,kl})Y_{kl}$$

$$= -\mathcal{E}_n^{(1)}B_m - \mathcal{E}_m^{(1)}B_n - \sum_k \mathcal{E}_{n,mk}^{(2)}B_k, \qquad (2.26)$$

$$i\frac{dN_{ij}}{d\tau} - \sum_m [(h_{im} - i\Gamma_{im})N_{mj} - N_{im}(h_{mj} + i\Gamma_{mj})]$$

$$+ i\sum_{mn} \bar{R}_{ij}^{mn}N_{mn} = -\mathcal{E}_i^{(1)}B_j^* + \mathcal{E}_j^{(1)}B_i, \qquad (2.27)$$

$$i\frac{dZ_{mn,j}}{d\tau} - \sum_{kl} (h_{mn,kl}^{(2)} - iR_{mn,kl})Z_{kl,j} + \sum_s (h_{sj} + i\Gamma_{sj})Z_{mn,s}$$

$$= -\mathcal{E}_m^{(1)}N_{nj} - \mathcal{E}_n^{(1)}N_{mj} - \sum_k \mathcal{E}_{m,nk}^{(2)}N_{kj} + \mathcal{E}_j^{(1)}Y_{mn}. \qquad (2.28)$$

Eqs. (2.25)–(2.28) constitute a closed system of equations for the third-order optical response, hereafter referred to as nonlinear exciton equations (NEE). These equations will be solved in the following section.

As outlined in Sec. I, in the absence of the dephasing (coherent dynamics) Eqs. (2.25) and (2.26) form a closed system of equations for the B and Y variables, obtained by factorizing $Z_{kl,n} = B_n^* Y_{kl}$ and $N_{lk} = B_k^* B_l$ in the right-hand side of Eq. (2.25). This system of equations has been first derived for Frenkel-excitons.[19,21] The analogous system of equations has been later rederived for semiconductor systems and generalized to higher-order responses.[29,35] Equations of motion for one- and two-exciton variables with phenomenological dephasing have been derived in Ref. 36. These equations can be recovered by setting $\bar{R} = 0$ in Eq. (2.27) which yields the same factorization. These equations, however, cannot fully describe pure dephasing effects in the propagation of exciton populations and coherences, which are of extreme importance in pump-probe and three-pulse photon echo spectroscopies. The SBE with dephasing[12] which constitute the powerful standard tool in time-domain spectroscopy of semiconductors treats dephasing processes properly. However, the two-exciton correlations are completely neglected. The NEE combine the advantages of both approaches and describe the combined effects of exciton dephasing, transport, and two-exciton correlations. In the next section we show how two-exciton correlations can be treated using the exciton-exciton scattering matrix.

III. GREEN'S FUNCTION EXPRESSIONS FOR OPTICAL RESPONSE

In this section we solve the NEE [Eqs. (2.25)–(2.28)] and derive Green's Function Expressions (GFE) for the optical response, establishing a nonlinear oscillator picture for the optical nonlinearities. Each of these equations contains a homogeneous part written in the left-hand side and an inhomogeneous source in the right-hand side. The solutions of these equations can be expressed using four Green's functions which are defined as the formal solution of Eqs. (2.25)–(2.28) when the right-hand side is replaced by a $\delta(t)$ source.

$$B_m(t) = \sum_n G_{mn}(t)B_n(0), \qquad (3.1)$$

$$Y_{mn}(t) = \sum_{m'n'} G_{mn,m'n'}^{(Y)}(t)Y_{m'n'}(0), \qquad (3.2)$$

$$N_{ij}(t) = \sum_{i'j'} G_{ij,i'j'}^{(N)}(t)N_{i'j'}(0), \qquad (3.3)$$

$$Z_{mn,j}(t) = \sum_{m'n'j'} G_{mn,j;m'n',j'}^{(Z)}(t)Z_{m'n',j'}(0). \qquad (3.4)$$

Here the one-exciton Green's function $G_{mn}(t)$ is given by

$$G_{mn}(t) = \theta(t)[\exp(-iht - \Gamma t)]_{mn}, \qquad (3.5)$$

where $\theta(t)$ is the Heaviside step function [$\theta(t) = 1$ for $t > 0$, and $\theta(t) = 0$ for $t < 0$]. The other Green's functions have similar expressions.

The linear polarization to first order in the driving field $\mathcal{E}(t)$ is given by

$$P^{(1)}(t) = \int_0^\infty dt_1 R^{(1)}(t_1)\mathcal{E}(t - t_1), \qquad (3.6)$$

where the linear response function obtained by solving Eq. (2.25) adopts the form

$$R^{(1)}(t) = i\sum_{mn} \mu_m^{(1)}\mu_n^{(1)}[G_{mn}(t) - G_{nm}^\dagger(t)]. \qquad (3.7)$$

Equation (2.8) implies that the third-order response is expressed as a sum of third-order terms in the expansion of B_n and $Z_{kl,m}$ in the driving field. The latter can be obtained by solving Eqs. (2.25)–(2.28) iteratively order by order in the driving field. This straightforward procedure yields analytical expressions for B_n and $Z_{kl,m}$ in terms of the Green's functions of Eqs. (2.25)–(2.28). It follows from Eq. (2.28) that the Green's function $G^{(Z)}(\tau)$ may be factorized as

$$G_{mn,k;m'n',k'}^{(Z)}(\tau) = G_{mn,m'n'}^{(Y)}(\tau)G_{k'k}^\dagger(\tau). \qquad (3.8)$$

This results from our simplified relaxation superoperator [Eq. (2.24)]. The only necessary Green's functions are therefore $G_{mn}(\tau)$, $G_{mn,m'n'}^{(Y)}(\tau)$, and $G_{mn,m'n'}^{(N)}(\tau)$ which can be found numerically by solving linear dynamical equations with no more than N^2 variables. The Green's function expressions (GFE) for the optical response derived in this way are presented in Appendix E. The crucial point in the present derivation is the factorization of the Green's function

$G^{(Z)}(\tau)$ [Eq. (3.8)] which follows from the factorized form of the relaxation operation [Eqs. (2.20)–(2.24)]. The GFE may not be obtained by directly factorizing the dynamical variables in the equations of motion (e.g., setting $\langle \hat{B}^\dagger \hat{B} \hat{B} \rangle = \langle \hat{B}^\dagger \rangle \langle \hat{B} \hat{B} \rangle$), as is commonly done.

We next turn to $G^{(Y)}$. It is well known that optical nonlinearities vanish for a system of harmonic oscillators (free bosons) provided the dipole operator is linear in the primary (boson) variables. The deviation of the system defined by Eqs. (2.2)–(2.5) from the harmonic oscillator system is determined by the matrix $U_{mn,kl}$ which describes anharmonic terms in the Hamiltonian, and the matrix $\mathcal{P}_{mn,kl}$ which reflects the deformation of the boson commutation relations. These induce exciton scattering processes which in turn give rise to optical nonlinearities. The combined effect of $\mathcal{P}$ and U can be conveniently described by the exciton scattering matrix. The nonlinear terms in the polarization operator [Eq. (2.8)] constitute an additional source of optical nonlinearity.

We start with the formal definition of the exciton scattering matrix $\bar{\Gamma}(t)$. To that end we first define the free-boson part $F_{mn,kl}(\tau)$ of the two-exciton Green's function by

$$F_{mk,nl}(\tau) \equiv G_{mn}(\tau) G_{kl}(\tau), \tag{3.9}$$

the exciton scattering matrix can be defined using the representation of the two-exciton Green's function $G^{(Y)}(t)$ in the form of the Bethe-Salpeter equation (see Appendix F). Using the tetradic operator form the Bethe-Salpeter equation reads

$$G^{(Y)}(t)(I-\mathcal{P}) = F(t) + \int_0^t d\tau'' \int_0^{\tau''} d\tau' F(t-\tau'')$$
$$\times \bar{\Gamma}(\tau'' - \tau') F(\tau'). \tag{3.10}$$

The matrix elements of Eq. (3.10) are given by Eq. (F5). Equation (3.10) represents $G^{(Y)}$ in terms of the exciton scattering matrix $\bar{\Gamma}$, which is calculated in Appendix F by switching to the frequency domain.

Finally we introduce the irreducible Green's function $\bar{G}_{mn,m'n'}(\tau)$ of Eq. (2.27) by

$$G^{(N)}_{mn,m'n'}(\tau) \equiv G_{mm'}(\tau) G^\dagger_{n'n}(\tau) + \bar{G}_{mn,m'n'}(\tau). \tag{3.11}$$

The first term represents the propagation of the $\langle \hat{B}^\dagger \hat{B} \rangle$ variable when they can be factorized as $\langle \hat{B}^\dagger \rangle \langle \hat{B} \rangle$. The second term represents therefore the genuine unfactorized propagation of the $\langle \hat{B}^\dagger \hat{B} \rangle$ variables. We are now in a position to obtain the GFE for the third-order optical response

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 R(t_3, t_2, t_1) \mathcal{E}(t-t_3)$$
$$\times \mathcal{E}(t-t_3-t_2) \mathcal{E}(t-t_3-t_2-t_1). \tag{3.12}$$

We first note that Eq. (E7) implies that the two-exciton Green's function $G^{(Y)}$ enters Eqs. (E6), (E10), and (E11) only through the product $G^{(Y)}(\tau)(I-\mathcal{P})$. The GFE can be obtained by substituting Eq. (3.10) into Eqs. (E6), (E10), and (E11) taking into account Eqs. (E9) and (E13). This yields GFE for $R(t_3, t_2, t_1)$ in terms of the one exciton Green's function G, the exciton scattering matrix $\bar{\Gamma}$, and the exciton-

population Green's function $\bar{G}$. The most general expression contains a large number of terms. However, in many cases the variables $\hat{B}_n$ in the Hamiltonian [Eqs. (2.2)–(2.8)] can be chosen such that $\mu^{(2)}_{m,kl} = 0$. The resulting expressions for the response function are simplified considerably in this case. If the transition dipoles μ_{01} and μ_{12} are perpendicular we need, however, to keep $\mu^{(2)}$. [Alternatively we can introduce three oscillator variables on each molecule Ref. (21).]

The GFE for $R(t_3, t_2, t_1)$ assume the following form

$$R(t_3, t_2, t_1) = \sum_{\alpha=1}^{3} R^c_\alpha(t_3, t_2, t_1) + \sum_{\alpha=1}^{2} R^i_\alpha(t_3, t_2, t_1) + \text{c.c.}, \tag{3.13}$$

where R^c is the coherent part of the response representing direct processes which do not involve $\bar{G}$

$R^c_1(t_3, t_2, t_1)$
$$= -i^3 \sum \mu^{(1)}_n \mu^{(1)}_k \mu^{(1)}_j \mu^{(1)}_m \int_0^{t_3} d\tau'' \int_0^{\tau''} d\tau'$$
$$\times G_{nn'}(t_3 + t_2 - \tau'') G_{kk'}(t_3 - \tau'')$$
$$\times G^\dagger_{j'j}(t_3 + t_2 + t_1 - \tau') G_{mm'}(\tau') \bar{\Gamma}_{m'j,nk}(\tau'' - \tau'), \tag{3.14}$$

$R^c_2(t_3, t_2, t_1)$
$$= -i^3 \sum \mu^{(1)}_n \mu^{(1)}_k \mu^{(1)}_j \mu^{(1)}_m \int_0^{t_3} d\tau'' \int_0^{\tau''} d\tau'$$
$$\times G_{nn'}(t_3 - \tau'') G_{kk'}(t_3 + t_2 + t_1 - \tau'')$$
$$\times G^\dagger_{j'j}(t_3 + t_2 - \tau') G_{mm'}(\tau') \bar{\Gamma}_{m'j,nk}(\tau'' - \tau'), \tag{3.15}$$

$R^c_3(t_3, t_2, t_1)$
$$= -i^3 \sum \mu^{(1)}_n \mu^{(1)}_k \mu^{(1)}_j \mu^{(1)}_m \int_0^{t_3 + t_2} d\tau'' \int_0^{\tau''} d\tau'$$
$$\times G_{nn'}(t_3 + t_2 + t_1 - \tau'') G_{kk'}(t_3 + t_2 - \tau'')$$
$$\times G^\dagger_{j'j}(t_3 - \tau') G_{mm'}(\tau') \bar{\Gamma}_{m'j,nk}(\tau'' - \tau'). \tag{3.16}$$

The sequential contributions R^i (which do depend on $\bar{G}$) are given by

$R^i_1(t_3, t_2, t_1)$
$$= 2 \sum \mu^{(1)}_m \mu^{(1)}_l \mu^{(1)}_k \mu^{(1)}_r \int_0^{t_3} d\tau'' \int_0^{\tau''} d\tau'$$
$$\times G_{ms}(\tau') \bar{\Gamma}_{js,i'r'}(\tau'' - \tau') G^\dagger_{j'j}(\tau'' - \tau')$$
$$\times G_{r'r}(t_3 - \tau'') \bar{G}_{i'j',kn}(t_3 + t_2 - \tau'') G^\dagger_{ln}(t_1), \tag{3.17}$$

$R^i_2(t_3, t_2, t_1)$
$$= 2 \sum \mu^{(1)}_m \mu^{(1)}_l \mu^{(1)}_k \mu^{(1)}_r \int_0^{t_3} d\tau'' \int_0^{\tau''} d\tau'$$
$$\times G_{ms}(\tau') \bar{\Gamma}_{js,i'r'}(\tau'' - \tau') G^\dagger_{j'j}(\tau'' - \tau')$$
$$\times G_{r'r}(t_3 - \tau'') \bar{G}_{i'j',nl}(t_3 + t_2 - \tau'') G_{nk}(t_1). \tag{3.18}$$

Equations (3.13)–(3.18) show how the time-domain nonlinear optical response is induced by exciton scattering. The coherent component R^c contains three contributions presented diagrammatically in Fig. 1. In all cases each of the three interactions with the optical field creates an exciton: two of these excitons are positive-frequency (pf) and their evolution is described by the Green's function G whereas the evolution of the third negative frequency (nf)-exciton is determined by the Green's function $G^\dagger$. The contributions presented in Figs. 1(a), 1(b) and 1(c) differ in that the exciton is produced by the first, the second and the third interactions with the field, respectively. The first scattering of the pf excitons occurs at $\tau = \tau'$; the last scattering at time $\tau = \tau''$. The last scattering although described by the same scattering amplitude, has a different nature compared to the previous ones: two pf excitons annihilate with the nf exciton, forming a single exciton which propagates by means of G to form the signal at $\tau = t$. Scattering between pf and nf excitons never occurs. $\bar{\Gamma}(\tau'' - \tau')$ describes the dynamics of two pf excitons between the first and the last scattering events.

The two sequential contributions are shown in Fig. 2. In Figs. 2(a) and 2(b) the nf exciton is created by the first and the second interaction with the field, respectively. After the second interaction we have one pf and nf exciton in both diagrams. Their coupled propagation due to phonon exchange is described by the Green's function $\bar{G}$. After the first scattering of the pf exciton, the phonon exchange is neglected since a stronger exciton-exciton scattering process takes place. Starting at $\tau = \tau'$ the system evolves in the same way as in the coherent case.

We have chosen to express the response function using the time intervals between consecutive interactions with the driving fields rather than the actual times of the interactions. This choice is particularly convenient for the incoherent component Eqs. (3.17) and (3.18). The three contributions to

the coherent part Eqs. (3.14)–(3.16) can be represented in a more concise form using the actual times: each of the three terms represents two out of six permutations of three times of interactions with the driving field. However, we are using the time intervals for the coherent parts as well since they are more suitable for the description of time-domain spectroscopies.

A notable advantage of this diagrammatic representation is that it allows us to immediately recognize the spatial direction of the various contributions. To that end, let us represent the fields in the form

$$\mathcal{E}(t) = \sum_j [\mathcal{E}_j(t)\exp(i\mathbf{k}_j\mathbf{r} - i\omega_j t)$$
$$+ \mathcal{E}_j^*(t)\exp(-i\mathbf{k}_j\mathbf{r} + i\omega_j t)]. \quad (3.19)$$

Within the rotating wave approximation, pf excitons are produced by the positive-frequency component $\mathcal{E}$ of the optical field whereas the nf exciton is produced by the negative-frequency component $\mathcal{E}^*$. This implies that the contributions shown in Figs. 1(a), 1(b), and 1(c) are proportional to $\mathcal{E}_1^*\mathcal{E}_2\mathcal{E}_3$, $\mathcal{E}_1\mathcal{E}_2^*\mathcal{E}_3$, and $\mathcal{E}_1\mathcal{E}_2\mathcal{E}_3^*$. Similarly, the two contributions in Figs. 2(a) and 2(b) are proportional to $\mathcal{E}_1^*\mathcal{E}_2\mathcal{E}_3$ and $\mathcal{E}_1\mathcal{E}_2^*\mathcal{E}_3$, respectively. It immediately follows then that each of the five signals will be generated only in a specific direction $\mathbf{k}_s$ as indicated in the figures.

The third-order optical response has been expressed in terms of the Green's function for the propagation of the two-exciton variables in Ref. 37. The GFE presented in this section are different in two respects. The first is purely formal: in the GFE the two-exciton propagation is expressed in terms of the exciton-exciton scattering matrix. Second, the expressions of Ref. 37 do not include the incoherent contribution [Eqs. (3.17) and (3.18)] which describes the evolution of the exciton populations and coherences.

IV. DISCUSSION

In this paper we have derived closed Green's function expressions (GFE) for the third-order optical response of an
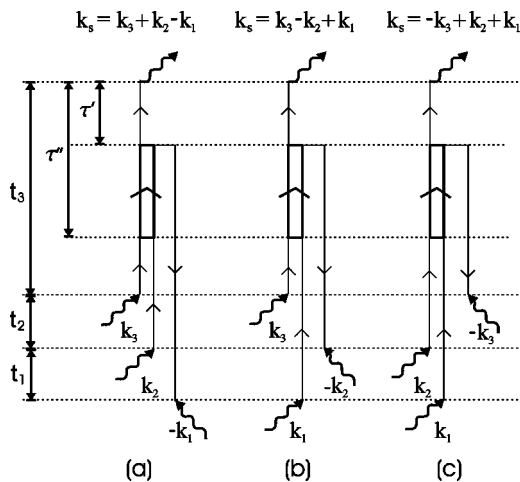

FIG. 1. Diagrammatic representation of the three contributions to the coherent part of the third-order optical response function $R^c(t_3, t_2, t_1)$ [(a) Eq. (3.14), (b) Eq. (3.15), and (c) Eq. (3.16)]. Time runs from the bottom to the top. A single line denotes the one-exciton Green's function G, the double line stands for the exciton scattering matrix $\bar{\Gamma}$. Arrows represent the three incoming fields and the signal field. An arrow pointing from left to right (right to left) implies that the incoming $\mathbf{k}_j$ field makes a $+\mathbf{k}_j$ ($-\mathbf{k}_j$) contribution to the signal wave vector $\mathbf{k}_s$.
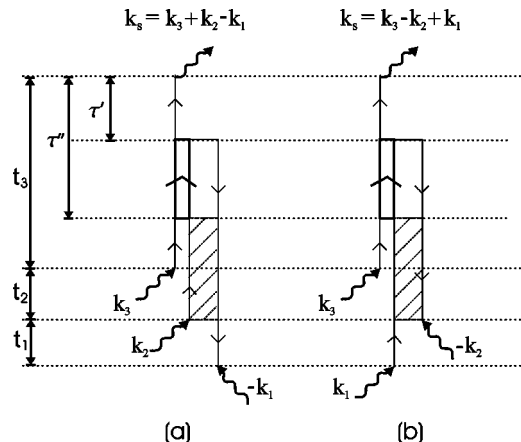

FIG. 2. The same as Fig. 1 but for the incoherent contribution $R^i(t_3, t_2, t_1)$ [(a) Eq. (3.17), (b) Eq. (3.18)]. The filled double line describes the irreducible part $\bar{G}$ of the Green's function representing the evolution of the exciton density matrix, i.e., the $N = \langle \hat{B}^\dagger \hat{B} \rangle$ variables.

excitonic system coupled to a phonon bath by solving the nonlinear exciton equations (NEE). The response is recast in terms of the exciton Green's function G, the exciton-exciton scattering matrix $\bar{\Gamma}$ and the Green's function $\bar{G}$ which describes incoherent exciton motion induced by the exciton-phonon scattering. Coupling to phonons is accounted for by relaxation kernels whereas optical nonlinearities originate from exciton-exciton scattering which is described by $\bar{\Gamma}$. The NEE provides a collective oscillator picture for exciton dynamics and the nonlinear response. For a linearly driven harmonic oscillator all nonlinear responses vanish. Optical nonlinearities are generated by the deviations from the linearly driven harmonic model which enter through anharmonicities, nonlinearities in the expansion of the polarization operator in powers of the primary variables, and the nonboson nature of the primary variables (deviations from boson statistics). The distinction between these three sources of optical nonlinearity depends on our choice of dynamical variables since transformations of variables change the commutation relations, the Hamiltonian and the polarization operator. It is possible, for example, to choose variables such that their commutation relations become those of bosons; such transformation to boson variables is known as bosonization. The classical limit of the bosonization procedure is the transformation to canonical variables (i.e., the variables in which the Poisson bracket has the canonical form). It can be shown that this classical transformation can always be extended to the bosonization of the original quantum system. Bosonization is a convenient tool for classifying the sources of optical nonlinearities as originating either from statistics or from anharmonicities: the former are described by nonlinear terms in the expansion of the polarization in boson operators whereas the latter are given by the anharmonic terms in the Hamiltonian. Bosonization is also a common tool for treating systems whose natural variables possess nontrivial commutation relations, i.e., spin systems,[38,39] electron-hole pairs,[40] and Frenkel excitons.[41] Bosonization was particularly popular at the early stages of condensed matter theory when diagrammatic perturbative expansions involved systems of free bosons as fermions as a reference.[42] Later it was shown[43] that nontrivial perturbation theories can be formulated for spin systems using the highly nonboson spin variables including nonzero temperatures. Nonboson commutation relations also do not pose a major difficulty in theories of nonlinear optical response of Frenkel exciton systems, which are based on equations of motion for one- and two-exciton variables.[15,19,28] In this paper we found the choice of dynamical variables that makes the polarization operator linear in the exciton variables to be the most adequate. These variables appear naturally for the two-band semiconductor model or for molecular aggregates made out of two-level molecules. For other systems (e.g., aggregates of three level molecules) this can be arranged by a proper transformation. This choice of variables greatly simplifies the GFE: the coherent contribution is represented by the product of four one-exciton Green's functions and the exciton scattering matrix, and the incoherent contribution has a simple form as well. Bosonization does not simplify the treatment, on the contrary it generates nonlinearities in the polarization operators and

the GFE becomes much more cumbersome.[44] This can be understood by recognizing that the dipole operator is the window through which the system interacts with the field. Bosonization tries to work with a basis set that is as close as possible to the system's eigenstates. However, the dipole operator, which has a particularly simple form in a zero-order basis set in real space, becomes quite complex in the eigenstate representation. A linear relationship between the dipole and the exciton variables makes the description of the wave packet created by the interactions with the field much more intuitive and compact.

The treatment of the optical response of semiconductors and molecular systems within the same unified framework allows us to establish a clear correspondence between different levels of theory developed for both types of systems. The simplest level which is based on keeping the $\langle \hat{B} \rangle$ variables alone is known as the SBE for the polarization in the theory of semiconductors[12] and the local field approximations (LFA) for Frenkel excitons.[15] Adding dephasing through relaxation kernels leads to the SBE for polarizations and populations for semiconductors, and equations of motion for the $\langle \hat{B} \rangle$ and $\langle \hat{B}^{\dagger} \hat{B} \rangle$ variables developed for Frenkel excitons.[17] The dynamics of $\langle \hat{B}^{\dagger} \hat{B} \rangle$ variables also describes the time- and frequency-resolved fluorescence.[24] The present article shows that the SBE and LFA theories are essentially the same. The proper accounting for two-exciton states has been first achieved by a scheme involving the $\langle \hat{B} \rangle$ and $\langle \hat{B} \hat{B} \rangle$ variables.[19] The corresponding equations for semiconductors were derived later.[29,35] The equivalence of these approaches has been established in Ref. 14 where the exciton representation for the two-band model was introduced. However, practical applications of this theory to semiconductors still constitute a nontrivial task because of the $\sim N^4$ scaling of the number of two-exciton state. Current applications are therefore limited to some crude approximate models of semiconductor superlattices which only take into account a few one- and two-exciton states[45] or to special systems such as semiconductor quantum wells in a strong magnetic field where the two-exciton manifold becomes manageable by virtue of the strong symmetry.[46]

The GFE expressions derived in this paper have no analogue in the semiconductor literature. Similar expressions have been derived earlier for aggregates made out of two-level molecules using Green's function techniques in the frequency domain with partial resummation of the principal contributions in exciton phonon coupling.[24] In this paper we have extended the GFE of Ref. 24 to a more general exciton system and derived them in a more intuitive way using the NEE and applying certain approximations for the relaxation kernels [Eqs. (2.20)–(2.24)] rather than factorization schemes for higher-order exciton variables. It is not possible to derive these expressions by factorizing the variables themselves. The present derivation clarifies the physical significance of the response function in the time domain, and should be particularly useful for the analysis of femtosecond measurements. The GFE describe the combined effects of exciton population-relaxations and coherent two-exciton motion, which is absolutely necessary for a proper description

of pump-probe and three-pulse photon echo spectroscopies. An expression that interpolates between the theories of Refs. 22 and 19 and incorporates both $\langle \hat{B}\hat{B} \rangle$ and $\langle \hat{B}^{\dagger}\hat{B} \rangle$ variables was derived in Ref. 23. The present theory is more general and the expressions are not additive in the contributions of both types of variables. The ability of the GFE to adequately describe femtosecond spectroscopy of molecular aggregates has been demonstrated by application to pump-probe spectra of the LH2 harvesting antenna of purple bacteria.[25] The theory presented here which avoids the explicit calculation of two-exciton states and allows us to make use of symmetries is an important step towards its application to realistic semiconductor materials as well.

The interpretation of optical nonlinearities in terms of exciton scattering is particularly useful for molecular aggregates. First, the local form of the U and $\mathcal{P}$ operators[28] and the form of the scattering matrix $\bar{\Gamma}$ given by Eq. (F10) implies that it can be obtained by inverting an $N \times N$ matrix rather than an $N^2 \times N^2$ tetradic matrix.[28] Second, this interpretation constitutes a real space picture of optical response which is very appealing: due to the local structure of the polarization operators[28] the driving field interacts with individual chromophores. This implies that aggregate structure can be directly probed using two-dimensional time-domain spectroscopy by examining the cross peaks in the double Fourier transforms of the response functions.[47] This is analogous to multidimensional NMR[48] and Raman echo[49] techniques.

ACKNOWLEDGMENTS

APPENDIX A: HAMILTONIAN FOR AN AGGREGATE OF MULTILEVEL MOLECULES

In this Appendix we sketch a derivation of the exciton representation [Eqs. (2.2)–(2.5)] for an arbitrary molecular aggregate. We consider a molecular aggregate made out of interacting multilevel molecules linearly coupled to a harmonic bath which represents intramolecular, intermolecular as well as solvent degrees of freedom. The Hamiltonian of the joint electronic and nuclear (bath) degrees of freedom can be written in the form

$$H = H_e[h(q)] + H_{\text{ph}}. \tag{A1}$$

Here $H_e[q]$ is the electronic part which depends on a set of parameters represented by h. H_{ph} is the phonon (bath) Hamiltonian representing a set of harmonic oscillators [see Eq. (2.3)]. The parameters h of the electronic Hamiltonian depend on the set of oscillator coordinates $q \equiv q_\alpha$. This dependence is the origin of the exciton-phonon coupling. We shall expand these parameters in a Taylor series around the equilibrium values $\bar{q}$ of the bath coordinates in the ground electronic state. We can then recast Eq. (A1) in a form of a generalized Davydov Hamiltonian:

$$H = H_e + H_{\text{ph}} + H_{\text{int}}, \tag{A2}$$

with

$$H_e \equiv H_e[\bar{q}], \tag{A3}$$

$$H_{\text{int}} = \sum_\alpha \left[\frac{\partial H_e[h]}{\partial h} \right]_{h=\bar{h}} \left[\frac{\partial h}{\partial q_\alpha} \right]_{q=0} q_\alpha. \tag{A4}$$

Equations (A1) and (2.3) express the total Hamiltonian H in terms of its electronic part H_e. To define H_e, we consider an assembly of $(N+1)$-level molecules. Assuming binary intermolecular interactions and using the basis set of molecular eigenstates, our most general Hamiltonian is

$$H_e = \sum_n \sum_i \Omega_n^i \rho_n^{ii} + \sum_{mn}^{m \neq n} \sum_{ij,kl} J_{mn}^{ij,kl} \rho_m^{ij} \rho_n^{kl}, \tag{A5}$$

where $\rho_n^{ij} \equiv |i\rangle_n {}_n\langle j|$ with $i,j = 0, \ldots, N$ is a complete set of operators for the nth molecule. The first term in Eq. (A5) describes the molecular Hamiltonians while the second term represents intermolecular interactions. The parameters denoted by h are now given by Ω_n^i and $J_{mn}^{ij,kl}$. The interaction Hamiltonian H_{int} can be written in a form

$$H_{\text{int}} = \sum_{ni} \sum_\alpha \bar{\Omega}_{n;\alpha}^i \rho_n^{ii} q_\alpha + \sum_{mn}^{m \neq n} \sum_{ij,kl} \sum_\alpha \bar{J}_{mn;\alpha}^{ij,kl} \rho_m^{ij} \rho_n^{kl} q_\alpha. \tag{A6}$$

Equation (A2) together with (2.3), (A5), and (A6) represent the most general Hamiltonian of a molecular aggregate linearly coupled to harmonic bath.

The aggregate driven by an external field $\mathcal{E}(\tau)$ is represented by the total Hamiltonian [Eq. (2.7)] with the polarization operator

$$P = \sum_n \sum_{ij} \mu_n^{ij} \rho_n^{ij}. \tag{A7}$$

The Hamiltonian [Eq. (A5)] can be simplified considerably by making use of the fact that the energy spacings between molecular levels $\triangle \Omega$ are usually much larger than typical values J of intermolecular interactions $J \ll \triangle \Omega$. However, there still might be closely lying levels. We shall therefore separate the molecular levels into groups using the following prescription: the energy spacings between any two levels within a group is not larger than $\sim J$, and the spacings between any two levels which belong to different groups is much larger than J. In the zeroth approximation, we can then neglect intermolecular couplings between levels which belong to different groups. The neglected terms can subsequently be taken into account perturbatively. The only exception is when, for example, the energy of a state whereby two molecules are excited in molecular states belonging to the same group is close to the energy of a state when a single molecule is excited to a molecular state which belongs to another group. The calculation then becomes tedious. As an example, we consider resonant third-order (four-wave mixing) nonlinear spectroscopy. In this case, we can pick up a single group of states on each molecule that can be resonantly excited from the ground state by a single interaction with the driving field. We will refer to these states as molecular single-excited (MSE) states. Another group of states participating in resonant third-order response are those that can be excited by a single interaction with the field starting

with one of the MSE states. In general, the states can be classified as either collective double-excitations (CDE) whereby two different molecules are excited or molecular double-excited (MDE) states, where a single molecule is excited to a molecular state which belongs to a group different from MSE. On each molecule we are now left with two groups of states: MSE and MDE. The aggregate states involved in third-order nonlinear are either singly excited (MSE) or doubly excited (either MDE or CDE). We can neglect couplings between these groups, which is a generalized Heitler–London approximation. The CDE and MDE are strongly coupled when the MDE energies lie within J from twice the energies of MSE. In summary, for resonant third-order nonlinear spectroscopy we can use a model with three groups of molecular states; the ground state, MSE, and MDE. There are three groups of the global aggregate states involved in the third-order response; the ground state, single-excited states and double excited states. These states are strongly coupled by intermolecular interactions within a group, the coupling between different groups can be neglected.

To establish the exciton oscillator picture of optical response, we introduce creation (annihilation) operators $\hat{B}_{nj}^{\dagger}(\hat{B}_{nj})$ of MSE where j denotes the jth MSE on the nth molecule. Denoting the ground state of the aggregate by $|\Omega\rangle$, we define $\hat{B}_{nj}^{\dagger}|\Omega\rangle$ to be a normalized single-excited state whereby the nth molecules are in the state $|j\rangle$, which belongs to MSE, and all other molecules are in the ground state. The states $\hat{B}_{nj}^{\dagger}|\Omega\rangle$ constitute the manifold of single-excited states of the aggregate. The CDE states are generated by $\hat{B}_{mj}^{\dagger}\hat{B}_{nj}^{\dagger}|\Omega\rangle$ for $m \neq n$. In order to treat the MDE and CDE in a similar manner and at the same time maintain an oscillator picture, we would like to avoid the introduction of additional operators; it is natural to represent the MDE states in a form $\hat{B}_{ni}^{\dagger}\hat{B}_{nj}^{\dagger}|\Omega\rangle$. Assuming that the number of MSE states is M we have $M(M+1)/2$ MDE states given by $\hat{B}_{ni}^{\dagger}\hat{B}_{mj}^{\dagger}|\Omega\rangle$.

APPENDIX B: EXCITON HAMILTONIAN FOR THE TWO-BAND MODEL

In this Appendix we derive the exciton representation [Eqs. (2.2)–(2.5)] for semiconductors, starting with the two-band Hamiltonian[12,50,51]

$$\hat{H} = \sum_{m_1 n_1} t_{m_1 n_1}^{(1)} \hat{a}_{m_1}^{\dagger} \hat{a}_{n_1} + \sum_{m_2 n_2} t_{m_2 n_2}^{(2)} \hat{b}_{m_2}^{\dagger} \hat{b}_{n_2}$$

$$+ \frac{1}{2} \sum_{m_1 n_1 k_1 l_1} V_{m_1 n_1 k_1 l_1}^{(1)} \hat{a}_{m_1}^{\dagger} \hat{a}_{n_1}^{\dagger} \hat{a}_{k_1} \hat{a}_{l_1}$$

$$+ \frac{1}{2} \sum_{m_2 n_2 k_2 l_2} V_{m_2 n_2 k_2 l_2}^{(2)} \hat{b}_{m_2}^{\dagger} \hat{b}_{n_2}^{\dagger} \hat{b}_{k_2} \hat{b}_{l_2}$$

$$+ \frac{1}{2} \sum_{m_1 n_2 l_1 k_2} W_{m_1 n_2 l_1 k_2} \hat{a}_{m_1}^{\dagger} \hat{b}_{n_2}^{\dagger} \hat{b}_{k_2} \hat{a}_{l_1}, \tag{B1}$$

where $\hat{a}_{n_1}(\hat{a}_{n_1}^{\dagger})$ and $\hat{b}_{n_2}(\hat{b}_{n_2}^{\dagger})$ are the annihilation (creation) Fermi operators of electrons and holes, respectively, satisfying the commutation relations

$$\hat{a}_{n_1}\hat{a}_{m_1}^{\dagger} + \hat{a}_{m_1}^{\dagger}\hat{a}_{n_1} = \delta_{m_1 n_1}, \quad \hat{b}_{n_2}\hat{b}_{m_2}^{\dagger} + \hat{b}_{m_2}^{\dagger}\hat{b}_{n_2} = \delta_{m_2 n_2}, \tag{B2}$$

and all the other anticommutators are zero. We adopt the following convention for indices: Latin indices with a subscript 1 (2), i.e., m_1 (m_2), stand for electrons (holes). A particle (electron-hole pair) is denoted by a Latin index with no subscript $m = (m_1 m_2)$.

The polarization operator P has the form

$$P \equiv \sum_{m_1 n_2} \mu_{m_1 n_2} (\hat{a}_{m_1}^{\dagger} \hat{b}_{n_2}^{\dagger} + \hat{b}_{n_2} \hat{a}_{m_1}). \tag{B3}$$

Following the derivation of Ref. 14 we introduce the particle (electron-hole) operators

$$\hat{B}_{m_1 m_2}^{\dagger} \equiv \hat{a}_{m_1}^{\dagger} \hat{b}_{m_2}^{\dagger}, \quad \hat{B}_{m_1 m_2} \equiv \hat{b}_{m_2} \hat{a}_{m_1}. \tag{B4}$$

We can express the commutation relations of particle operators as well as the Hamiltonian in terms of an infinite series of normally ordered operators $\hat{B}^{\dagger}$ and $\hat{B}$. This can be accomplished in the following way. Expressing the commutation relations of $\hat{B}$ and $\hat{B}^{\dagger}$ in terms of the electron and the hole operators $\hat{a}, \hat{b}, \hat{a}^{\dagger}$, and $\hat{b}^{\dagger}$ we can project the Hamiltonian and the right-hand side (rhs) of the commutation relations into the subspaces with the given number of excitations. We then make an ansatz and assume that the Hamiltonian and the commutation relations can be expanded in a power series involving normally ordered products of operators. Because the Hamiltonian conserves the number of particles, each term should contain an equal number of creation $\hat{B}^{\dagger}$ and annihilation $\hat{B}$ operators. We can easily determine the expansion coefficients starting with the zero-order terms (in $\hat{B}$ and $\hat{B}^{\dagger}$), making use of the fact that an operator $\hat{B}^{\dagger} \ldots \hat{B}^{\dagger} \hat{B} \ldots \hat{B}$ which contains n creation and n annihilation operators is zero on all the subspace of state containing less than n excitations. This method allows us to determine the coefficients successively, order by order. For calculating the third-order response, we need to expand the Hamiltonian up to the fourth order and the commutation relations up to the second order.[22] The total Hamiltonian is finally given by Eqs. (2.2)–(2.8), with

$$h_{mn} \equiv t_{m_1 n_1}^{(1)} \delta_{m_2 n_2} + \delta_{m_1 n_1} t_{m_2 n_2}^{(2)} + W_{m_1 m_2 n_1 n_2}, \tag{B5}$$

$$U_{mn,kl} \equiv -\frac{1}{4} [t_{m_1 k_1}^{(1)} \delta_{m_2 k_2} \delta_{n_1 l_1} \delta_{n_2 l_2} + \delta_{m_1 k_1} t_{m_2 k_2}^{(2)} \delta_{n_1 l_1} \delta_{n_2 l_2}$$

$$+ \delta_{m_1 k_1} \delta_{m_2 k_2} t_{n_1 l_1}^{(1)} \delta_{n_2 l_2} + \delta_{m_1 k_1} \delta_{m_2 k_2} \delta_{n_1 l_1} t_{n_2 l_2}^{(2)}]$$

$$+ \frac{1}{4} [V_{m_1 n_1 k_1 l_1}^{(1)} \delta_{m_2 k_2} \delta_{n_2 l_2}$$

$$+ \delta_{m_1 k_1} \delta_{n_1 l_1} V_{m_2 n_2 k_2 l_2}^{(2)}], \tag{B6}$$

and $\mathcal{P}$ in Eq. (2.5) represents the deviation from particle boson statistics and is given by

$$\mathcal{P} = \frac{1}{2} [\mathcal{P}^{(1)} + \mathcal{P}^{(2)}]. \tag{B7}$$

Here $\mathcal{P}^{(1)}(\mathcal{P}^{(2)})$ is the electron (hole) permutation operator:

$$\mathcal{P}^{(1)}_{mn,pq} \equiv \delta_{m_1 q_1} \delta_{p_1 n_1} \delta_{m_2 p_2} \delta_{n_2 q_2},$$

$$\mathcal{P}^{(2)}_{mn,pq} \equiv \delta_{m_2 q_2} \delta_{p_2 n_2} \delta_{m_1 p_1} \delta_{n_1 q_1}. \tag{B8}$$

The parameters $\bar{h}_{mn;\alpha}$ and $\bar{U}_{mn,kl;\alpha}$ may be derived in a similar way.

APPENDIX C: ELIMINATION OF PHONON VARIABLES

In this Appendix we derive expressions for the relaxation terms $\dot{B}_m, \dot{Y}_{mn}, \dot{N}_{nj}$, and $\dot{Z}_{nm,j}$ which enter Eqs. (2.11)–(2.14). The relaxation superoperators will be calculated perturbatively to second order in the exciton-phonon coupling. Our calculation is based on equations of motion for phonon-assisted variables. The projection operator technique will be used to justify a factorization scheme which allows us to close the system of equations. To set the stage we note that the full system-bath density matrix $\hat{\rho}$ can be represented in a form

$$\hat{\rho} = \rho^{(0,0)}(\mathbf{q})|\Omega\rangle\langle\Omega| + \sum_m \rho_m^{(1,0)}(\mathbf{q})\hat{B}_m^\dagger|\Omega\rangle\langle\Omega|$$

$$+ \sum \rho_{mn}^{(2,0)}(\mathbf{q})\hat{B}_m^\dagger\hat{B}_n^\dagger|\Omega\rangle\langle\Omega| + \sum_{nm} \rho_{m,n}^{(1,1)}(\mathbf{q})\hat{B}_m^\dagger|\Omega\rangle$$

$$\times\langle\Omega|\hat{B}_n + \sum_{mnj} \rho_{mn,j}^{(2,1)}(\mathbf{q})\hat{B}_m^\dagger\hat{B}_n^\dagger|\Omega\rangle\langle\Omega|\hat{B}_j + \text{H.c} \tag{C1}$$

In Eq. (C1) $|\Omega\rangle$ denotes the ground state of the exciton system, $\mathbf{q} = (q_{\alpha L}, q_{\alpha R})$ represents the nuclear variables in Liouville space where L and R stand for left and right variables of nuclear wave packets $\rho^{(i,j)}(\mathbf{q})$, and the index α parametrizes nuclear oscillators [Eq. (2.3)].

Higher-order terms in $\hat{B}$ and $\hat{B}^\dagger$ are omitted in Eq. (C1) since they are not involved in the third-order optical response. The projection operator technique starts by introducing the projection operators $\hat{\mathcal{P}}$ and $\hat{\mathcal{Q}}$ with

$$\hat{\mathcal{Q}} \equiv I - \hat{\mathcal{P}}. \tag{C2}$$

We define $\hat{\mathcal{P}}$ as an operator acting in the nuclear space with

$$\hat{\mathcal{P}}\rho^{(i,j)}(\mathbf{q}) \equiv \rho_0(\mathbf{q})\text{Tr}_{\mathbf{q}}[\rho^{(i,j)}(\mathbf{q})], \tag{C3}$$

where $\rho_0(\mathbf{q})$ is the equilibrium nuclear wave packet in the ground electronic state. Since to zeroth order in exciton-phonon coupling the nuclear motions are uncoupled we have

$$\hat{\rho}(\tau) = \hat{\mathcal{P}}\hat{\rho}(\tau). \tag{C4}$$

Applying Eq. (C4) to Eq. (C1) implies that to zeroth order in exciton phonon coupling the following factorization holds

$$\langle \hat{B}_{i_1}^\dagger \ldots \hat{B}_{i_n}^\dagger \hat{B}_{j_1} \ldots \hat{B}_{j_m} p_{\alpha_1} \ldots p_{\alpha_r} q_{\beta_1} \ldots q_{\beta_s} \rangle$$

$$= \langle \hat{B}_{i_1}^\dagger \ldots \hat{B}_{i_n}^\dagger \hat{B}_{j_1} \ldots \hat{B}_{j_m} \rangle \text{Tr}_{\mathbf{q}}[p_{\alpha_1} \ldots p_{\alpha_r} q_{\beta_1} \ldots q_{\beta_s} \rho_0(\mathbf{q})]. \tag{C5}$$

We have applied the projection operator technique to derive Eq. (C5). The derivation involves equations of motion

for phonon assisted variables which will be closed using Eq. (C5). The projection operator technique will not be used hereafter.

Substituting Eq. (2.4) into Eq. (2.10) we obtain the relaxation terms which enter Eqs. (2.11)–(2.14) in a form:

$$\dot{B}_m = \sum \bar{h}_{mn,\alpha} B_{n;\alpha}^{(q)} + \sum \bar{V}_{mn,kl;\alpha} Z_{kl,n;\alpha}^{(q)}, \tag{C6}$$

$$\dot{Y}_{mn} = \sum \bar{h}_{mn,kl;\alpha}^{(2)} Y_{kl;\alpha}^{(q)}, \tag{C7}$$

$$\dot{N}_{ij} = \sum (\bar{h}_{im,\alpha} N_{mj;\alpha}^{(q)} - N_{im;\alpha}^{(q)} \bar{h}_{mj,\alpha}), \tag{C8}$$

$$\dot{Z}_{mn,j} = \sum (\bar{h}_{mn,kl;\alpha}^{(2)} Z_{kl,j;\alpha}^{(q)} - Z_{mn,i;\alpha}^{(q)} \bar{h}_{ij,\alpha}), \tag{C9}$$

where $\bar{V}_{mn,kl;\alpha}$ and $\bar{h}_{mn,kl;\alpha}^{(2)}$ are defined by

$$\bar{V}_{mn,kl;\alpha} \equiv 2\bar{U}_{mn,kl;\alpha} - 2\sum_p \mathcal{P}_{mn,pk} \bar{h}_{pl,\alpha}$$

$$-2\sum_{pq} \mathcal{P}_{mn,pq} \bar{U}_{pq,kl;\alpha}, \tag{C10}$$

$$\bar{h}_{mn,kl;\alpha}^{(2)} \equiv \delta_{mk} \bar{h}_{nl,\alpha} + \bar{h}_{mk,\alpha} \delta_{nl} + \bar{V}_{mn,kl;\alpha}. \tag{C11}$$

In Eqs. (C6)–(C9) we have introduced the phonon-assisted variables

$$B_{n;\alpha}^{(s)} \equiv \langle \hat{B}_n X_\alpha^{(s)} \rangle, \qquad Y_{mn;\alpha}^{(s)} \equiv \langle \hat{B}_m \hat{B}_n X_\alpha^{(s)} \rangle,$$

$$N_{mn;\alpha}^{(s)} \equiv \langle \hat{B}_n^\dagger \hat{B}_m X_\alpha^{(s)} \rangle, \qquad Z_{mn,j;\alpha}^{(s)} \equiv \langle \hat{B}_j^\dagger \hat{B}_m \hat{B}_n X_\alpha^{(s)} \rangle, \tag{C12}$$

with $s = p, q; X_\alpha^{(q)} \equiv q_\alpha, X_\alpha^{(p)} \equiv p_\alpha$.

To obtain the relaxation terms we use equations of motion for the phonon-assisted variables [Eq. (C12)]. The rhs of these equations will contain the phonon assisted variables, exciton variables [Eq. (2.9)] and new variables of the form $\langle \hat{B}_n X_\alpha^{(s)} X_\beta^{(s')} \rangle, \langle \hat{B}_m \hat{B}_n X_\alpha^{(s)} X_\beta^{(s')} \rangle, \langle \hat{B}_m^\dagger \hat{B}_n X_\alpha^{(s)} X_\beta^{(s')} \rangle$, and $\langle \hat{B}_j^\dagger \hat{B}_m \hat{B}_n X_\alpha^{(s)} X_\beta^{(s')} \rangle$. However, all new variables come with coefficients proportional to the exciton-phonon coupling. It is clearly seen from Eqs. (C6)–(C9) that in order to obtain the relaxation terms in second order in the coupling, the phonon-assisted variables should be calculated in first order. This implies that the new variables should be taken in zeroth order and we can apply the factorization of Eq. (C5) which closes the equations. After applying the factorization of Eq. (C5), the equations of motion for the phonon-assisted variables can be represented in a form

$$i\frac{dX_\alpha^{(s)}}{d\tau} = iv_\alpha X_\alpha^{(-s)} - i\delta_{sp} \sum \bar{h}_{mn,\alpha} N_{nm}, \tag{C13}$$

$$i\frac{dB_{m;\alpha}^{(s)}}{d\tau} - \sum h_{mn}B_{n;\alpha}^{(s)} - iv_\alpha B_{m;\alpha}^{(-s)}$$

$$= \sum \bar{h}_{mn;\alpha}w_\alpha^{(s)}B_n + \sum V_{mn,kl}Z_{kl,n;\alpha}^{(s)}$$

$$+ \sum \bar{V}_{mn,kl;\alpha}w_\alpha^{(s)}Z_{kl,n} - \mathcal{E}_m^{(1)}X_\alpha^{(s)}$$

$$- \sum \mathcal{E}_{m,kl}^{(2)}N_{lk;\alpha}^{(s)} - \sum \mathcal{E}_{m,kl}^{(3)}Y_{kl;\alpha}^{(s)}, \qquad \text{(C14)}$$

$$i\frac{dY_{mn;\alpha}^{(s)}}{d\tau} - \sum h_{mn,kl}^{(2)}Y_{kl;\alpha}^{(s)} - iv_\alpha Y_{mn;\alpha}^{(-s)}$$

$$= \sum \bar{h}_{mn,kl;\alpha}^{(2)}w_\alpha^{(s)}Y_{kl} - \mathcal{E}_n^{(1)}B_{m;\alpha}^{(s)} - \mathcal{E}_m^{(1)}B_{n;\alpha}^{(s)}$$

$$- \sum \mathcal{E}_{n,mk}^{(2)}B_{k;\alpha}^{(s)}, \qquad \text{(C15)}$$

$$i\frac{dN_{ij;\alpha}^{(s)}}{d\tau} - \sum (h_{im}N_{mj;\alpha}^{(s)} - N_{im;\alpha}^{(s)}h_{mj}) - iv_\alpha N_{ij;\alpha}^{(-s)}$$

$$= \sum (\bar{h}_{im;\alpha}w_\alpha^{(s)}N_{mj} - w_\alpha^{(s)}N_{im}h_{mj}) - i\delta_{sp}N_{im}\bar{h}_{mj;\alpha}$$

$$- \mathcal{E}_i^{(1)}B_{j;\alpha}^{(s)}* + \mathcal{E}_j^{(1)}B_{i;\alpha}^{(s)}, \qquad \text{(C16)}$$

$$i\frac{dZ_{mn,j;\alpha}^{(s)}}{d\tau} - \sum (h_{mn,kl}^{(2)}Z_{kl,j;\alpha}^{(s)} - Z_{mn,i;\alpha}^{(s)}h_{ij}) - iv_\alpha Z_{mn,j;\alpha}^{(-s)}$$

$$= \sum w_\alpha^{(s)}(\bar{h}_{mn,kl;\alpha}^{(2)}Z_{kl,j} - Z_{mn,i}\bar{h}_{ij;\alpha})$$

$$- i\delta_{sp}\sum \bar{h}_{kj;\alpha}Z_{mn,k} - \mathcal{E}_m^{(1)}N_{nj;\alpha}^{(s)} - \mathcal{E}_n^{(1)}N_{mj;\alpha}^{(s)}$$

$$- \sum \mathcal{E}_{m,nk}N_{kj;\alpha}^{(s)} + \mathcal{E}_j^{(1)}Y_{mn;\alpha}^{(s)}, \qquad \text{(C17)}$$

where we have used the notation $(-p)\equiv(q), (-q)\equiv(p)$ and

$$v_\alpha^{(q)} \equiv m_\alpha^{-1}, \quad v_\alpha^{(p)} = -m_\alpha\omega_\alpha^2,$$

$$w_\alpha^{(q)} \equiv \text{Tr}_\mathbf{q}[q_\alpha q_\alpha \rho_0(\mathbf{q})] = \frac{1}{2m_\alpha\omega_\alpha}\coth\left(\frac{\beta\omega_\alpha}{2}\right), \qquad \text{(C18)}$$

$$w_\alpha^{(p)} \equiv \text{Tr}_\mathbf{q}[p_\alpha q_\alpha \rho_0(\mathbf{q})] = -\frac{i}{2},$$

with $\beta=(kT)^{-1}$, T being the temperature.

Equations (C13)–(C17) constitute a closed system of equations for the phonon-assisted variables $B^{(s)}, Y^{(s)}, N^{(s)}$, and $Z^{(s)}$. The relaxation terms are obtained in Appendix D upon substituting the solutions of Eqs. (C13)–(C17) into Eqs. (C6)–(C9).

APPENDIX D: PHONON-INDUCED RELAXATION SUPEROPERATORS

In this Appendix we solve Eqs. (C6)–(C9) and (C13)–(C18) for the relaxation terms which yield closed expressions for the relaxation operators.

We start by noting that Eqs. (C13)–(C17) can be formally written in the operator form:

$$i\frac{dA_\alpha^{(q)}}{d\tau} - hA_\alpha^{(q)} - \frac{i}{m_\alpha}A_\alpha^{(p)} = W_\alpha^{(q)}(\tau),$$

$$i\frac{dA_\alpha^{(p)}}{d\tau} - hA_\alpha^{(p)} + im_\alpha\omega_\alpha^2 A_\alpha^{(q)} = W_\alpha^{(p)}(\tau), \qquad \text{(D1)}$$

where $A_\alpha^{(s)}$ denotes the variables $X_\alpha^{(s)}, B_\alpha^{(s)}, Y_\alpha^{(s)}, N_\alpha^{(s)}$, and $Z_\alpha^{(s)}$; $W_\alpha^{(s)}$ is the rhs of the corresponding equation, whereas h is the linear operator representing the free evolution of each variable (in the absence of relaxation). Each of the variables has a different h, as can be seen from Eqs. (C13)–(C17). We further introduce the set of the Green's functions of these operators which satisfy the equations

$$i\frac{d\mathcal{G}}{d\tau} - h\mathcal{G} = i\delta(\tau). \qquad \text{(D2)}$$

The solution of Eq. (D1) can be represented in a form

$$A_\alpha^{(q)}(\tau) = -i\int_0^\infty dt\Bigg[\cos(\omega_\alpha t)\mathcal{G}(t)W_\alpha^{(q)}(\tau-t)$$

$$+ \frac{1}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)\mathcal{G}(t)W_\alpha^{(p)}(\tau-t)\Bigg],$$

$$A_\alpha^{(p)}(\tau) = -i\int_0^\infty dt[\cos(\omega_\alpha t)\mathcal{G}(t)W_\alpha^{(p)}(\tau-t)$$

$$- m_\alpha\omega_\alpha\sin(\omega_\alpha t)\mathcal{G}(t)W_\alpha^{(q)}(\tau-t)]. \qquad \text{(D3)}$$

It follows from Eq. (D2) that the Green's functions $\mathcal{G}(\tau)$ satisfy the condition

$$\mathcal{G}(\tau')\mathcal{G}(\tau'') = \mathcal{G}(\tau'+\tau''). \qquad \text{(D4)}$$

Since $\mathcal{G}(\tau)$ describes the evolution of the exciton variables alone, the Green's functions $\mathcal{G}_{ij,mn}^{(N)}$ and $\mathcal{G}_{ij,k;mn,r}^{(Z)}$ related to the variables N_{ij} and $Z_{ij,k}$, respectively, can be expressed in terms of the Green's functions $\mathcal{G}_{mn}$ and $\mathcal{G}_{mn,kl}^{(Y)}$ which are related to B_m and Y_{mn} variables (one-exciton and two-exciton Green's functions):

$$\mathcal{G}_{ij;mn}^{(N)} = \mathcal{G}_{im}(\tau)\mathcal{G}_{nj}^\dagger(\tau),$$

$$\mathcal{G}_{ij,k;mn,r}^{(Z)}(\tau) = \mathcal{G}_{ij,mn}^{(Y)}(\tau)\mathcal{G}_{rk}^\dagger(\tau). \qquad \text{(D5)}$$

Equations (C13)–(C17) may be solved as follows: we first solve Eq. (C14) taking into account only the first-order in the driving field terms. Using Eq. (D3) we find $\bar{B}_\alpha^{(s)}$ ($\bar{B}_\alpha^{(s)}$ is the first-order contribution in the driving field to $B_\alpha^{(s)}$) in terms of B. We then substitute $\bar{B}_\alpha^{(s)}$ into Eqs. (C15) and (C16). Solving Eqs. (C15) and (C16) by applying Eq. (D3) we express $Y_\alpha^{(s)}$ and $N_\alpha^{(s)}$ in terms of B, Y, N, and the driving field. We then substitute $N_\alpha^{(s)}$ and $Y_\alpha^{(s)}$ in Eq. (C17) and solve Eq. (C17) which yields $Z_\alpha^{(s)}$ in terms of B, Y, N, Z, and the driving field. We next solve Eq. (C14) and substitute $X_\alpha^{(s)}$ together with $N_\alpha^{(s)}, Y_\alpha^{(s)}$, and $Z_\alpha^{(s)}$ found earlier into Eq. (C14). By solving Eq. (C14) we obtain the contribution to $B_\alpha^{(s)}$ to third-order in the driving field. After finishing this straightforward but tedious procedure we express the phonon assisted variables $B_\alpha^{(q)}, Y_\alpha^{(q)}, N_\alpha^{(q)}$, and $Z_\alpha^{(q)}$ in terms of the

exciton variables B, Y, N, Z, and the driving field. These expressions involve the one- and two-exciton Green's functions $\mathcal{G}_{mn}(\tau)$ and $\mathcal{G}^{(Y)}_{mn,kl}(\tau)$ as well as the phonon Green's functions $M_{\alpha}(\tau)$ defined by

$$M_{\alpha}(\tau) \equiv \frac{1}{2m_{\alpha}\omega_{\alpha}}\left[\coth\left(\frac{\beta\omega_{\alpha}}{2}\right)\cos(\omega_{\alpha}\tau) - i\sin(\omega_{\alpha}\tau)\right]. \tag{D6}$$

The relaxation terms are obtained by substituting these expressions into Eqs. (C6)–(C9). These expressions for the relaxation terms involve the one- and two-exciton Green's functions $\mathcal{G}$ and $\mathcal{G}^{(2)}$ as well as the collective (bath) coordinate Green's functions $M^{(ij)}(\tau)$ with $i, j = 1, 2, 3$ defined by

$$M^{(ij)}(\tau) \equiv \sum_{\alpha} \bar{h}^{(i)}_{\alpha} \otimes \bar{h}^{(j)}_{\alpha} M_{\alpha}(\tau), \tag{D7}$$

where we have defined $\bar{h}^{(1)}_{mn;\alpha} \equiv \bar{h}_{mn,\alpha}$, $\bar{h}^{(3)}_{mn,kl;\alpha} \equiv \bar{V}_{mn,kl;\alpha}$, and $\bar{h}^{(2)}_{mn,kl;\alpha}$ has been defined earlier [Eq. (C11)]. For example

$$M^{(1,3)}_{mn;ij,kl} = \sum_{\alpha} \bar{h}_{mn,\alpha} \bar{V}_{ij,kl;\alpha} M_{\alpha}(\tau). \tag{D8}$$

The phonon Green's functions $M^{(ij)}(\tau)$ can be conveniently expressed in terms of tensor spectral densities $C^{(i,j)}(\omega)$:

$$M^{(i,j)}(\tau) = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}C^{(i,j)}(\omega)$$
$$\times\left[\coth\left(\frac{\beta\omega}{2}\right)\cos(\omega\tau) - i\sin(\omega\tau)\right]. \tag{D9}$$

with the spectral densities defined by

$$C^{(i,j)}(\omega) = \sum_{\alpha} \frac{1}{2m_{\alpha}\omega_{\alpha}}\bar{h}^{(i)}_{\alpha} \otimes \bar{h}^{(j)}_{\alpha}$$
$$\times 2\pi[\delta(\omega - \omega_{\alpha}) - \delta(\omega + \omega_{\alpha})]. \tag{D10}$$

In what follows we first neglect the relaxation terms involving the driving field. The remaining relaxation terms can be recast in the following form:

$$\dot{B}_m(\tau) = \sum \int_0^{\infty} dt R^{B,B}_{m;n}(t) B_n(\tau - t), \tag{D11}$$

$$\dot{Y}_{mn}(\tau) = \sum \int_0^{\infty} dt R^{Y,Y}_{mn;kl}(t) Y_{kl}(\tau - t), \tag{D12}$$

$$\dot{N}_{ij}(\tau) = \sum \int_0^{\infty} dt R^{N,N}_{ij;mn}(t) N_{mn}(\tau - t), \tag{D13}$$

$$\dot{Z}_{mn,j}(\tau) = \sum \int_0^{\infty} dt R^{Z,Z}_{mn,j;kl,i}(t) Z_{kl,i}(\tau - t). \tag{D14}$$

The relaxation superoperators in Eqs. (D11)–(D14) have the form:

$$R^{B,B}_{m;n}(t) = -i\sum \mathcal{G}_{m'n'}(t) M^{(1,1)}_{mm';n'n}(t), \tag{D15}$$

$$R^{Y,Y}_{mn,kl}(t) = -i\sum \mathcal{G}^{(Y)}_{m'n',k'l'}(t) M^{(2,2)}_{mn,m'n';kl,k'l'}(t), \tag{D16}$$

$$R^{N,N}_{mn,kl}(t) = -i\sum \mathcal{G}_{m'k'}(t)\mathcal{G}^{\dagger}_{l'n'}(t)[\delta_{ll'}\delta_{n'n}M^{(1,1)}_{mm',k'k}(t)$$
$$- \delta_{mm'}\delta_{ll'}M^{(1,1)}_{n'n,k'k}(t) + \delta_{k'k}\delta_{m'm}$$
$$\times M^{(1,1)}_{n'n,ll'}(-t) - \delta_{k'k}\delta_{n'n}M^{(1,1)}_{mm',ll'}(-t)]. \tag{D17}$$

Invoking the Markov approximation, we obtain Eqs. (2.20)–(2.23) where the relaxation superoperators Γ_{mn}, $R_{mn,kl}$ and $\bar{R}^{mn}_{ij}$ are defined by

$$\Gamma_{mn} \equiv \sum_{n'} \int_0^{\infty} dt R^{B,B}_{m;n'}(t)\mathcal{G}^{\dagger}_{n'n}(t), \tag{D18}$$

$$R_{mn,kl} \equiv \sum_{m'n'} \int_0^{\infty} dt R^{Y,Y}_{mn;m'n'}(t)\mathcal{G}^{(Y)\dagger}_{m'n',kl}(t), \tag{D19}$$

$$\bar{R}^{mn}_{ij} \equiv \sum_{m'n'} \int_0^{\infty} dt R^{N,N}_{ij;m'n'}(t)\mathcal{G}^{\dagger}_{m'm}(t)\mathcal{G}_{n'n}(t). \tag{D20}$$

Equation (D18) can be derived as follows: neglecting relaxation, $B_n(\tau - t)$ is given by

$$B_n(\tau - t) \cong \sum_{n'} \mathcal{G}^{\dagger}_{nn'}(t) B_{n'}(\tau). \tag{D21}$$

Substituting this into the rhs of Eq. (D11) results immediately in Eq. (2.20) together with Eq. (D18). Equations (D19) and (D20) are obtained in a similar way. The zero-order Green's functions [Eq. (D2)] represent the free evolution when the relaxation terms are neglected. The effect of these Green's functions in Eqs. (D18)–(D20) can be interpreted as a transformation to a rotating frame.[15,16]

APPENDIX E: GREEN'S FUNCTION EXPRESSION FOR NONLINEAR OPTICAL RESPONSE FUNCTIONS

In this Appendix we derive expressions for the time-domain third order response function $R(t_3, t_2, t_1)$ which connects the third-order polarization $P^{(3)}(\tau)$ with the driving field [Eq. (3.12)]. To that end, we need to evaluate $B_n(\tau)$ and $Z_{kl,m}(\tau)$ to third order in the driving field $\mathcal{E}(\tau)$ and substitute them into Eq. (2.8). We first find the first-order term $B_n^{(1)}(\tau)$ using Eq. (2.25)

$$B_n^{(1)}(\tau) = i\int_0^{\infty} dt \sum_m G_{nm}(t)\mathcal{E}^{(1)}_m(\tau - t) . \tag{E1}$$

Hereafter all summations are performed over repeating indices. Substituting $B_n(\tau)$ obtained from Eq. (E1) into Eqs. (2.28) and (3.11), we obtain the second-order terms of $Y_{mn}(\tau)$ and $N_{ij}(\tau)$:

$$Y_{mn}(\tau) = i^2\int_0^{\infty} dt_2\int_0^{\infty} dt_1 \sum_{m'n'kk'} G^{(Y)}_{mn,m'n'}(t_2)G_{k'k}(t_1)$$
$$\times \bar{\mathcal{E}}^{(1)}_{m'n',k'}(\tau - t_2)\mathcal{E}^{(1)}_k(\tau - t_2 - t_1), \tag{E2}$$

$$N_{ij}(\tau) = -i^2 \int_0^\infty dt_2 \int_0^\infty dt_1 \sum \{G_{ii'}(t_2+t_1)G_{j'j}^\dagger(t_2)\mathcal{E}_{j'}^{(1)}(\tau-t_2)\mathcal{E}_{i'}^{(1)}(\tau-t_2-t_1) + G_{ii'}(t_2)G_{j'j}^\dagger(t_2+t_1)\mathcal{E}_{j'}(\tau-t_2-t_1)$$

$$\times \mathcal{E}_{i'}^{(1)}(\tau-t_2) + \bar{G}_{ij,i'j'}(t_2)[G_{i'm'}(t_1)\delta_{j'n'} + \delta_{i'n'}G_{m'j'}^\dagger(t_1)]\mathcal{E}_{n'}^{(1)}(\tau-t_2)\mathcal{E}_{m'}^{(1)}(\tau-t_2-t_1)\}, \tag{E3}$$

where we have used Eq. (3.11) and introduced the notation

$$\bar{\mathcal{E}}_{mn,k}^{(1)} \equiv \mathcal{E}_n^{(1)}\delta_{mk} + \mathcal{E}_m^{(1)}\delta_{nk} + \mathcal{E}_{n,mk}^{(2)} . \tag{E4}$$

The third-order term in $Z_{mn,j}$ is obtained upon substitution of Eqs. (E2) and (E3) into Eq. (2.28) and making use of Eq (3.8). A convenient representation is obtained by introducing a response function $\hat{Z}_{mn,j}(t_3,t_2,t_1)$ by

$$Z_{mn,j}(\tau) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \hat{Z}_{mn,j}(t_3,t_2,t_1)\mathcal{E}(\tau-t_3)\mathcal{E}(\tau-t_3-t_2)\mathcal{E}(\tau-t_3-t_2-t_1), \tag{E5}$$

which adopts a form

$$\hat{Z}_{mn,j}(t_3,t_2,t_1) = -i^3 \sum \{G_{mn,m'n'}^{(Y)}(t_3+t_2)G_{j'j}^\dagger(t_3)G_{k'k}(t_1)\mu_{j'}^{(1)}\bar{\mu}_{m'n',k'}^{(1)}\mu_k^{(1)} + G_{mn,m'n'}^{(Y)}(t_3)G_{j'j}^\dagger(t_3+t_2)$$

$$\times G_{ii'}(t_2+t_1)\bar{\mu}_{m'n',i}^{(1)}\mu_{j'}^{(1)}\mu_{i'}^{(1)} + G_{mn,m'n'}^{(Y)}(t_3)G_{j'j}^\dagger(t_3+t_2+t_1)G_{ii'}(t_2)\bar{\mu}_{m'n',i}^{(1)}\mu_{i'}^{(1)}\mu_{j'}^{(1)}$$

$$+ G_{mn,m'n'}^{(Y)}(t_3)G_{j'j}^\dagger(t_3)\bar{G}_{i'j',i''j''}(t_2)[G_{i''k}(t_1)\delta_{j''l} + \delta_{i''l}G_{kj''}^\dagger(t_1)]\bar{\mu}_{m'n',i'}^{(1)}\mu_l^{(1)}\mu_k^{(1)}\}, \tag{E6}$$

where we have used the notation

$$\bar{\mu}_{mn,k}^{(1)} \equiv \mu_n^{(1)}\delta_{mk} + \mu_m^{(1)}\delta_{nk} + 2\mu_{k,mn}^{(2)} - 2\sum \mathcal{P}_{nm,kj}\mu_j^{(1)} - 2\sum \mathcal{P}_{nm,rs}\mu_{k,rs}^{(2)}. \tag{E7}$$

Substituting Eqs. (E2), (E3), (E5) and (E6) into Eq. (2.25), we obtain

$$B_m^{(3)}(\tau) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \hat{B}_m(t_3,t_2,t_1)\mathcal{E}(\tau-t_3)\mathcal{E}(\tau-t_3-t_2)\mathcal{E}(\tau-t_3-t_2-t_1), \tag{E8}$$

with

$$\hat{B}_m(t_3,t_2,t_1) = \hat{B}_m^{(1)}(t_3,t_2,t_1) + \int_0^{t_3} dt \hat{B}_m^{(2)}(t,t_3-t,t_2,t_1), \tag{E9}$$

and

$$\hat{B}_m^{(1)}(t_3,t_2,t_1) = -i^3 \sum \{G_{mm'}(t_3)G_{ii'}(t_2+t_1)G_{j'j}^\dagger(t_2)\bar{\mu}_{m',ji}^{(2)}\mu_{j'}^{(1)}\mu_{i'}^{(1)} + G_{mm'}(t_3)G_{ii'}(t_2)G_{j'j}^\dagger(t_2+t_1)\bar{\mu}_{m',ji}^{(2)}\mu_{i'}^{(1)}\mu_{j'}^{(1)}$$

$$+ G_{mm'}(t_3)\bar{G}_{ij,i'j'}(t_2)[G_{i'l}(t_1)\delta_{j'k} + \delta_{i'k}G_{lj'}^\dagger(t_1)]\bar{\mu}_{m',ji}^{(2)}\mu_k^{(1)}\mu_l^{(1)} - G_{mm'}(t_3)$$

$$\times G_{kl,k'l'}^{(Y)}(t_2)G_{j'j}(t_1)\mu_{m',kl}^{(2)}\bar{\mu}_{k'l',j'}^{(1)}\mu_j^{(1)}\}, \tag{E10}$$

$$\hat{B}_m^{(2)}(t,t_3-t,t_2,t_1) = i^4 \sum V_{sj,kl}\{G_{ms}(t)G_{kl,n'm'}^{(Y)}(t_3+t_2-t)G_{j'j}^\dagger(t_3-t)G_{k'k''}(t_1)\mu_{j'}^{(1)}\bar{\mu}_{n'm',k'}^{(1)}\mu_{k''}^{(1)} + G_{ms}(t)$$

$$\times G_{kl,n'm'}^{(Y)}(t_3-t)G_{j'j}^\dagger(t_3+t_2-t)G_{ii'}(t_2+t_1)\bar{\mu}_{n'm',i}^{(1)}\mu_{j'}^{(1)}\mu_{i'}^{(1)} + G_{ms}(t)G_{kl,n'm'}^{(Y)}(t_3-t)$$

$$\times G_{j'j}^\dagger(t_3+t_2+t_1-t)G_{ii'}(t_2)\bar{\mu}_{n'm',i}^{(1)}\mu_{i'}^{(1)}\mu_{j'}^{(1)} + G_{ms}(t)G_{kl,n'm'}^{(Y)}(t_3-t)G_{j'j}^\dagger(t_3-t)\bar{G}_{i'j',i''j''}(t_2)$$

$$\times [G_{i''k'}(t_1)\delta_{j''l'} + \delta_{i''l'}G_{k'j''}^\dagger(t_1)]\bar{\mu}_{n'm',i'}^{(1)}\mu_{l'}^{(1)}\mu_{k'}^{(1)}\}. \tag{E11}$$

Here we have used the following notation:

$$\bar{\mu}_{m,kl}^{(2)} \equiv 2\mu_{l,km}^{(2)} - 2\sum \mathcal{P}_{mk,nl}\mu_n^{(1)} - 2\sum \mathcal{P}_{mk,rs}\mu_{l,rs}^{(2)}. \tag{E12}$$

The response function adopts the final form

$$R(t_3,t_2,t_1) = \sum \mu_n^{(1)}\hat{B}_n(t_3,t_2,t_1)$$

$$+ \sum \mu_{j,mn}^{(2)}\hat{Z}_{mn,j}(t_3,t_2,t_1). \tag{E13}$$

APPENDIX F: THE EXCITON SCATTERING MATRIX

In this Appendix we derive a closed expression for the exciton scattering matrix $\bar{\Gamma}$. To get it in a simpler form we

first include the relaxation operators for one- and two-exciton variables in the matrices h_{mn} and $U_{mn,kl}$. To that end we represent the two-exciton relaxation matrix $R_{mn,kl}$ in a form

$$R_{mn,kl} = \delta_{mk}\Gamma_{nl} + \Gamma_{mk}\delta_{nl} + 2\tilde{R}_{mn,kl}$$
$$- 2\sum_{\mathcal{P}} \mathcal{P}_{mn,kp}\Gamma_{pl} - 2\sum_{pq} \mathcal{P}_{mn,pq}\tilde{R}_{pq,kl}, \quad (F1)$$

and introduce the renormalized matrices $\hat{h}$ and $\hat{U}$ by

$$\hat{h}_{mn} \equiv h_{mn} - i\Gamma_{mn}, \quad (F2)$$

$$\hat{U}_{mn,kl} \equiv U_{mn,kl} - i\tilde{R}_{mn,kl}, \quad (F3)$$

where $\hat{V}$ is expressed in terms of $\hat{U}$ and $\hat{h}$ by [see Eq. (2.16)]

$$\hat{V}_{mn,kl} \equiv 2\hat{U}_{mn,kl} - 2\sum_{p} \mathcal{P}_{mn,pk}\hat{h}_{pl} - 2\sum_{pq} \mathcal{P}_{mn,pq}\hat{U}_{pq,kl}. \quad (F4)$$

Equations (2.25)–(2.28) can then be rearranged by eliminating the relaxation terms Γ and R while substituting the renormalized values of $\hat{h}$ and $\hat{U}$ given by Eqs. (F2)–(F4). In what follows we will only use the renormalized values. The tetradic scattering matrix $\bar{\Gamma}$ is defined by Eq. (3.10). In matrix form it reads

$$\sum_{k'l'} G^{(Y)}_{mn,k'l'}(t)(\delta_{k'k}\delta_{l'l} - \mathcal{P}_{k'l',kl})$$
$$= F_{mn,kl}(t) + \sum_{m'n'k'l'} \int_0^t d\tau'' \int_0^{\tau''} d\tau' F_{mn,m'n'}(t-\tau'')$$
$$\times \bar{\Gamma}_{m'n',k'l'}(\tau''-\tau') F_{k'l',kl}(\tau'), \quad (F5)$$

Equation (3.10) can be easily solved by switching to the frequency domain

$$\bar{\Gamma}(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t}\bar{\Gamma}(\omega), \quad (F6)$$

where it assumes the form

$$G^{(Y)}(\omega)(I-\mathcal{P}) = F(\omega) + F(\omega)\bar{\Gamma}(\omega)F(\omega), \quad (F7)$$

yielding

$$\bar{\Gamma}(\omega) = -[F(\omega)]^{-1} + [F(\omega)]^{-1}G^{(Y)}(\omega)(I-\mathcal{P})$$
$$\times [F(\omega)]^{-1}. \quad (F8)$$

In the frequency domain we have

$$G(\omega) = (\omega - \hat{h})^{-1}, \quad F(\omega) = (\omega - \hat{h}\otimes I + I\otimes\hat{h})^{-1}, \quad (F9)$$

$$G^{(Y)}(\omega) = [\omega - (I-\mathcal{P})(I\otimes\hat{h} + \hat{h}\otimes I) - 2(I-\mathcal{P})\hat{U}]^{-1}.$$

Substituting Eqs. (F9) into Eq. (F8) yields

$$\bar{\Gamma}(\omega) = [I + \mathcal{P}\hat{h}_0^{(2)}F(\omega) - 2(I-\mathcal{P})\hat{U}F(\omega)]^{-1}$$
$$\times [-\omega\mathcal{P} + 2(I-\mathcal{P})\hat{U}]. \quad (F10)$$

where $\hat{h}_0^{(2)}$ is the free-boson part of the two-exciton Hamiltonian with matrix element

$$\hat{h}_0^{(2)} \equiv \hat{h}\otimes I + I\otimes\hat{h}. \quad (F11)$$

Equations (F6) and (F10) form a closed expression for the exciton scattering matrix.

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